



Application of Ni supported over mixed Mg–Al oxides to crystal violet wet air oxidation: The role of the reaction conditions and the catalyst

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ABSTRACT

This study explores the ability of nickel catalysts supported over Mg–Al mixed oxides (Ni/HT) by incipient wetness impregnation technique for the catalytic wet air oxidation of aqueous crystal violet solutions. The effect of operational conditions such as temperature, pressure, pH, presence of the catalyst and initial dye concentration has been tested. It has been demonstrated that Ni/HT is an efficient catalyst for the CWAO of crystal violet (CV) at mild reaction conditions. The reaction which was carried out at its natural pH, showed to be the most efficient when Ni/HT was employed. The catalyst does not lose any of its activity in the recycling experiments performed, when CV degradation is considered.

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1. Introduction

Intensive research aiming at reducing the pollution in industrial wastewaters has been performed during the last decades. Among the studied techniques, wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) appear as two of the most promising wastewater treatments. A wide range of products have already been treated successfully due to the ability of this process to eliminate compounds with low solubility such as polymers or fatty acids [1]. More specifically, CWAO has already been proved to be an efficient process to destroy dyes in aqueous solutions [2,3].

In WAO processes, the generation of active oxygen species, such as hydroxyl radicals, takes place at high temperatures and pressures. This process is known to have a great potential for the treatment of effluents containing a high content of organic matter or contaminants for which direct biological purification is unfeasible [4]. The WAO process has well-known capacities for breaking down biologically refractory compounds to simpler, easily treatable materials before they are released into the environment. In general, this aqueous phase flameless combustion process takes place at high reaction temperatures (473–593 K) and pressures (20–200 bar) by means of active oxygen species, such as hydroxyl radicals [5].

The main drawback of WAO is the high operating costs, as a consequence of the high reaction temperature and pressure previously mentioned. Thus, the efficiency of WAO can be considerably improved by the use of catalysts, either in the form of solids or as homogeneous catalysts. Waste minimization is linked with the reaction selectivity; therefore proper choice of the catalyst plays a decisive role. Compared to conventional WAO, CWAO has lower energy requirements. Due to the presence of a catalyst, much higher oxidation rates are achieved compared to WAO, and consequently, milder reaction conditions can be used.

Hydrotalcites (HT), or layered double hydroxides (LDHs), are anionic clays. The structure of the HT is very similar to brucite $\text{Mg}(\text{OH})_2$, where an isomorphous substitution of Mg^{2+} by a trivalent element M^{3+} occurs. When Mg^{2+} ions are replaced by a trivalent ion, a net positive charge is compensated by anions in the inter-layer. The hydrotalcite-like compounds are generally described by the general formula $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}[\text{A}^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$ where M is the metal and A the anion. Anionic clays based on HT have arisen considerable interest because of the diversity of their chemical compositions and those uncountable applications such as catalysts, catalysts supports, ion exchangers, stabilizers and adsorbents [6]. A large number of hydrotalcite-like compounds have been extensively studied as precursors, since they permit a rather suitable dispersion for the metal catalyst. Ni/Al mixed oxides have shown remarkable properties as catalysts precursors such as high metal dispersion and stability against sintering, even under extreme conditions [7].

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Co-precipitated Ni–Mg–Al hydrotalcite has been found to be active for the liquid phase oxidation of alcohols with molecular oxygen [8], while supported iron oxide catalyst prepared from Mg–Al hydrotalcite revealed the high activity for ethylbenzene dehydrogenation [9] and for dyes treatments [10]. The high activities of all these catalysts are undeniable due to the stable and highly dispersed active metal species [11].

Crystal violet (CV) is a triarylmethane dye which is employed as a component of blue and black inks for printing, ball-pens, dyeing paper and finally as a colourant for non-food products such as fertilizers, anti-freezes and detergents. In this work, we aimed at preparing nickel catalysts supported over Mg–Al mixed oxides by incipient wetness impregnation technique for the CWAO of CV to study the catalyst effect on the process efficiency. The effect of operational conditions such as temperature, pressure, pH and initial dye concentration will also be tested.

2. Experimental

2.1. Materials

CV was selected as the model pollutant because it is hardly biodegradable by the conventional biological processes, but widely employed in the textile, colour solvent, ink, paint, paper, pharmaceutical and plastic industries. The dye was purchased from Sigma–Aldrich (Steinheim, Germany) and used without further purification. The main characteristics of this dye and its structure are shown in Table 1.

2.2. Preparation of the catalyst

HT precursor was used as support in the preparation of nickel catalysts. It was prepared by co-precipitation. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma–Aldrich, Steinheim, Germany) in desired amounts were dissolved in 600 mL of water to form solution A. Besides, Na_2CO_3 and NaOH were mixed in 300 mL of water to form solution B. Solution B was stirred for 1 h at constant temperature of 65 °C. Then, solution A was slowly dropped forming a precipitate [12]. The resulting solution was aged at 60 °C for 18 h. Then, they were filtered and washed with distilled water at 40 °C for 2 h. The resulting was dried at 100 °C for 12 h.

Nickel catalyst was prepared by incipient wetness impregnation technique employing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ purchased from Panreac (Barcelona, Spain) in aqueous solution as precursor. The precursor amount was calculated to obtain a catalyst load of 7 wt% of nickel in the final analysis. The resulting solid was calcined at 550 °C for 5 h.

2.3. Characterization

The characterization of the support and catalyst were carried out by physical adsorption of nitrogen at 77 K in a Micromeritics ASAP 2010 apparatus. X-ray-powder diffraction (XRD) patterns of support and catalyst before and after calcination were recorded by a diffractometer SIEMENS D-501. The metal loading was determined by means of X-ray fluorescence (XRF) (Broker S4 Explorer). The reducibility of the calcined samples was studied by temperature programmed reduction TPR in a TPDRO 1100 ThermoFinnigan, employing a classical system with thermal conductivity detector TCD in order to determine the consumption of H_2 from a H_2/Ar mixture. Typically, a sample of 5 mg of each calcined catalyst was heated up in a linear temperature program of 5 °C/min up to 950 °C in the flow of the reaction mixture (5% H_2/Ar , 8.5 mL min^{−1}). After the reduction, the catalyst was cooled down in situ in the H_2/Ar flow. As soon as the temperature was below 40 °C, the reduced catalyst was passivated for 30 min in a flow of a 5% O_2/He mixture. Then the sample was reduced again under the conditions of the previous reduction but at a heating rate of 10 °C/min. Before each reduction, the baseline was allowed to stabilize and adjusted to zero. On the basis of the TPR results, it was possible to measure the nickel dispersion as a ratio of nickel reduced after passivation to the total amount of reducible nickel after calcination as determined by TPR [13].

2.4. Catalytic wet air oxidation experiments

Experiments were conducted in a Hastelloy high-pressure Microreactor C-276 Autoclave Engineers with a volume of 100 mL. The reactor (i.d. 5 cm) was equipped with an electrically heated jacket, a turbine agitator, a variable speed magnetic drive and a valve for sampling. The temperature and the stirring speed were controlled by means of a PID controller. The gas inlet, gas release valve, pressure gauge, rupture disk and cooling water feed line were situated on the top of the reaction vessel, whereas the liquid sample line and the thermocouple were immersed in the reaction mixture.

The reactor was first loaded with 100 mL of commercial dye solution with (0.5 g) or without catalyst, and initially pressurized with nitrogen to ensure inert atmosphere. Afterwards, the system was heated to the desired temperature. The reactor is then pressurized with air and samples were withdrawn periodically after sufficient flushing of the sample line. Pressure drop was monitored and additional oxygen was charged in order to maintain a constant total pressure throughout the duration of the test. During the reactions, samples were taken at regular intervals to measure total organic carbon (TOC), dye content and toxicity.

Table 1
Main characteristics of crystal violet.

Dye	Structure	CAS number	CI number	Molecular weight (g mol ^{−1})	Molecular formulae	λ_{max} (nm)
Crystal violet		548-62-9	42555	407.98	$\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$	588

Table 2
Catalyst and support characterization.

	Metal content (nickel weight%)		BET area, m ² /g	Metallic dispersion, %
	Intended	Observed		
Ni/MgAl	7.0	6.8	169.0	26.7
HT	–	–	182.0	

2.5. Procedures and analysis

Dye concentration was determined at the wavelength corresponding to its maximum UV–vis absorption (Table 1), which was monitored by a Shimadzu UV–vis spectrophotometer. TOC measurements were carried out in a Shimadzu TOC analyzer, after filtration (pore diameter 10 mm) to assess the degree of total oxidation. For evaluation of catalytic activity, colour and TOC removal efficiency were calculated as the ratio between the colour and TOC measured at each instant and the values of this parameter for the initial solution. Since TOC analysis provides only information about the removal of total organic carbon from the liquid-phase, selectivity towards non-organic compounds (S_{NOC}) was defined as $100(X_{\text{TOC}}/X_{\text{dye}})$ where X_{TOC} and X_{dye} are TOC and dye conversion respectively.

HPLC analyses were performed in a Varian Prostar-230 apparatus with a C18. The flow rate of the mobile phase was set at 1.0 mL min^{−1}. Solvent A was 25 mM aqueous ammonium acetate buffer (pH 6.9), while solvent B was methanol. A linear gradient was set as follows: $t=0$, $C=95$; $t=20$, $C=50$; $t=45$, $C=10$; $t=50$, $C=95$.

The ecotoxicity of the liquid effluent was measured with a Microtox 500 Analyzer on samples before and after decoloration according to the test protocols defined by the manufacturer (Azur Environmental, Newark, Del.) with the Microtox data analysis program (Microtox Omni Software). This bioassay is based on the decrease of light emission by *Vibrio fischeri* as the result of its exposure to a toxicant according to ISO 11348-2. The pH of the samples was adjusted to 7.0 ± 0.5 . Percentage inhibition of the bioluminescence was obtained mixing 0.5 mL of the final effluent of each experiment and 0.5 mL of the luminescent bacterial suspension. The toxicity of each sample was expressed as the percent of the inhibition of the luminescence relative to a non-contaminated blank (Milli-Q water). Results are given in toxicity units (TU).

3. Results and discussion

3.1. Catalyst characterization

The nickel loadings of calcined solids are presented in Table 2 where Ni/MgAl is the impregnated and calcined catalyst. A divergence of 0.2% of nickel content from the intended value can be observed. It is noticeable that metallic dispersion reaches a 26.7%. The specific surface area of the catalyst shifted towards lower values with the addition of Ni due to the blockage of pores after the impregnation and reconstruction of the phases [14].

Fig. 1 shows the XRD powder patterns of the support and catalyst dried at 100 °C, where all samples presented the characteristics reflections lines at (003), (006), (009), (015), (018), (110) and (113) corresponding to layered double hydroxide (LDH) structure, and no different crystalline phases were detected, indicating that the inclusion of Ni by wetness impregnation does not affect to the HT structure [14,15].

It is known that the crystallographic transition from the lamellar to mixed oxide structures in the hydrotalcite takes place progressively in a wide range of temperature. TG-DTA analysis showed that for samples calcined at 550 °C the LDH structure collapses

to form a Mg–Al spinel [16]. When a LDH is calcined below 700 °C, only the metal oxide of the metallic cation present in major amount will be detected [17]. Accordingly, in each sample, only a poorly crystallized MgO phase was detected at $2\theta=43^\circ$ and 62° , due to the fact that aluminium ions also occupy the octahedral sites in the MgO lattice. The XRD pattern of the as-prepared Ni/MgAl catalyst exhibits no obvious differences from the one of pure MgAl support, indicating that nickel cations are well dispersed, forming a solid solution [18]. The presence of the nickel was confirmed by XRF analysis. The diffraction lines of Ni/HT coincided with those of the as-prepared HT support and no other lines of Ni containing species were discerned.

Regarding the N₂ adsorption isotherms of Ni/MgAl 550 °C for 4 h, all samples exhibited type IV isotherms, characteristic of mesoporous materials according to the IUPAC classification [19].

TPR profile of NiO prepared from decomposition of Ni(NO₃)₂ by calcination at 800 °C for 5 h showed one sharp peak centered at 398 °C while the Ni/MgAl catalyst showed two peaks at 515 and 800 °C. The reducibility may depend on the degree of aggregation of the nickel oxide. A fine distribution of the nickel oxide will result in a stronger interaction with each other and then a higher reduction temperature [20]. A TPR peak assigned to nickel oxides that are not completely integrated in the spinel structure, but have a certain degree of interaction with the support has been observed at 505 °C approximately [21]. As also reported, a high temperature above 800 °C was required to reduce the stoichiometric nickel aluminate spinels [22].

3.2. Catalytic performances

3.2.1. Blank tests

The synthesized catalyst was tested in the batch reactor. The results are shown in Fig. 2. At 120 °C, in the absence of the catalyst (WAO), a 1% conversion was observed. A slight improvement was displayed when the calcined MgAl support was added in comparison to the WAO experiment, enhancing TOC removal to 18%. One may also notice a TOC removal of 16% at zero time for the

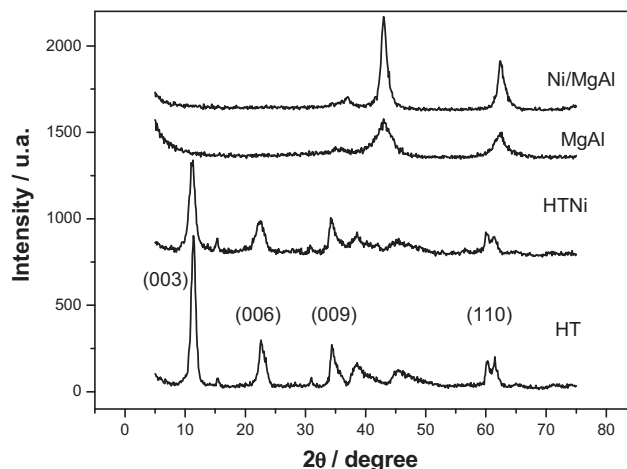


Fig. 1. Powder X-ray diffraction patterns of the calcined and uncalcined HT compounds.

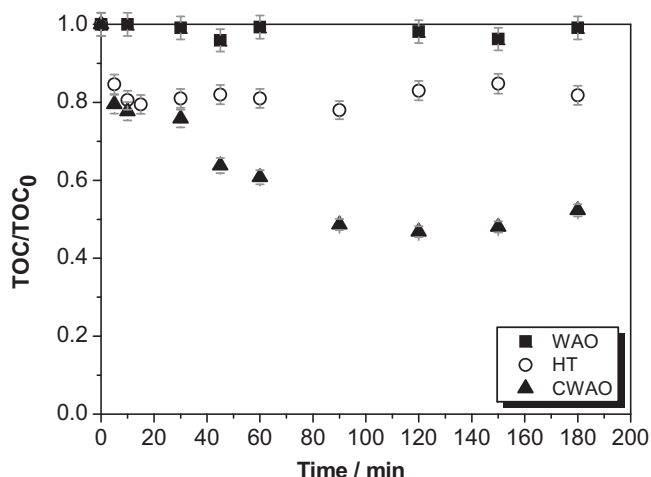


Fig. 2. Batch experiments without catalyst (WAO), in the presence of the calcined hydrotalcite support (MgAl) and the catalyst (Ni/MgAl) at 120 °C, 50 bar, 100 ppm.

reactions conducted in the presence of the solids (MgAl or Ni/MgAl) was obtained, which is probably due to an adsorption effect. However, in the presence of the nickel catalyst Ni/MgAl, the removal rate of TOC was significantly enhanced with respect to the WAO process, reaching a conversion of 48% at 120 °C. This shows that the presence of a Ni/MgAl catalyst significantly improves the performance of the oxidation process and the poor effect of the support.

3.2.2. Effect of temperature on the activity of Ni/HT in the WAO and CWAO of CV

The efficiency of the oxidation of CV aqueous solutions was tested in terms of two usually adopted indicators for global degradation performance: colour bleaching by removal of the most intense absorption peak at 588 nm and TOC removal.

The influence of the reaction temperature was studied under 50 bar in the range of 120–220 °C (Fig. 3a and b).

The results showed that CV removal was very sensitive to the temperature. The effect of the temperature was much more remarkable for the WAO process (Fig. 3a) as at 120 °C the CV conversion is up to 20% whereas at 220 °C CV conversion reaches the 95% within the 15 first minutes of the reaction. From the Arrhenius plot for the evolution of the initial CV conversion rate as a function of temperature, the apparent activation energy for both processes was calculated. It was found to be 81.38 and 11.15 kJ mol⁻¹ for WAO and CWAO reaction, respectively. This proves the efficacy of the presence of the Ni/MgAl catalyst for CV removal. In addition, reaction order of crystal violet in CWAO was calculated to be 0.5 with the temperature. In the case of WAO, the CV removal follows first

order kinetic, proving that the effect of the temperature is higher when no catalyst is employed.

The same conclusions could be drawn for total organic carbon abatement. In this case, temperature had a great impact in both processes (wet air oxidation and catalytic wet air oxidation). These results showed that TOC conversion increased with the temperature in the range of 120–220 °C from 0.9% to 51.4% in the WAO process and from 47.7% to 88.6%, respectively in the CWAO reaction (Fig. 3b). It can be noticed that the conversion for the reaction at 220 °C without catalyst is almost the same than that for the catalytic reaction at 120 °C, showing that the presence of the catalyst allows milder reaction conditions for the same conversion degree.

Looking at the pH evolution in Fig. 3c it is noticeable that the pH reaches more basic values for the CWAO due to the basic nature of the catalyst, which basifies the media. In both cases it can be noticed that pH become more acidic, mostly detected at high temperatures. This implies that carboxylic and other acids are probably formed during the oxidation of the organic matter. Analysis in a C18 column confirmed the presence of traces of formic and acetic acid.

Fig. 4a and b shows the spectrum of WAO and CWAO reaction at 120 °C respectively. Experimental results indicated that CV could be degraded efficiently in the presence of the catalyst, as the peak at 588 nm vanishes totally at the end of the reaction. On the other hand, for the non-catalytic reaction, the degradation of the CV was notably less efficient, as it can be seen in Fig. 4a. The concentration of the dye decreased with time, reaching a conversion of 21% and 97% at the end of the WAO and CWAO reaction, respectively. Additionally, the characteristic wavelengths shifted slightly from 588 to 572 nm in the WAO reaction and from 588 to 567 nm in the catalytic reaction. This hypsochromic shift of the absorption band was possible due to the formation of a series of N-de-methylated intermediates in a step-wise manner [19], which is stronger in the catalytic reaction, suggesting that the oxidation of the formed intermediates is enhanced in the presence of a catalyst. It is worth mentioning that the removal of CV occurs much faster than the degradation of intermediate carbon due to the easy removal of the peripheral methyl groups.

Fig. 4c and d shows the spectrum of WAO and CWAO reaction at 200 °C. In the case of the WAO reaction an increase in the reaction temperature led to a final conversion of CV of 93%, whereas in the CWAO reaction, total conversion is attained at 120 min. In the case of CWAO it can be observed that the formation of new absorption bands between 330 and 372 nm is more intense which can be interpreted as the formation of new intermediates compounds, indicating that the catalytic reaction goes through a different pathway as it has been checked by HPLC analysis.

A simple exponential function, $f(t) = Ae^{-kt}$, was fitted to each curve. Differentiation of the expressions at $t=0$ gave the initial reaction rates of TOC removal. These reaction rates in TOC removal

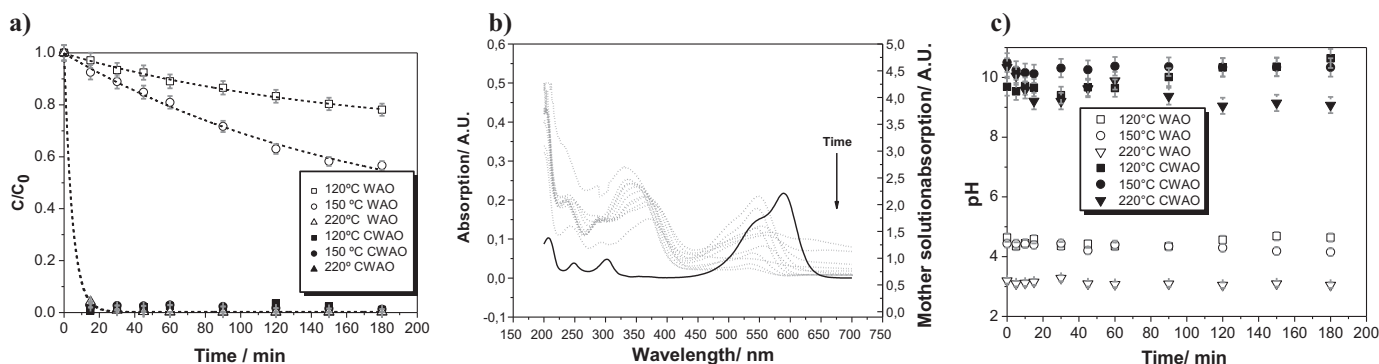


Fig. 3. Evolution of the (a) CV conversion (b) TOC conversion in the WAO and CWAO of crystal violet with the temperature at 50 bar and 100 ppm. (c) Evolution of the pH in the WAO and CWAO of CV with the temperature at 50 bar and 100 ppm.

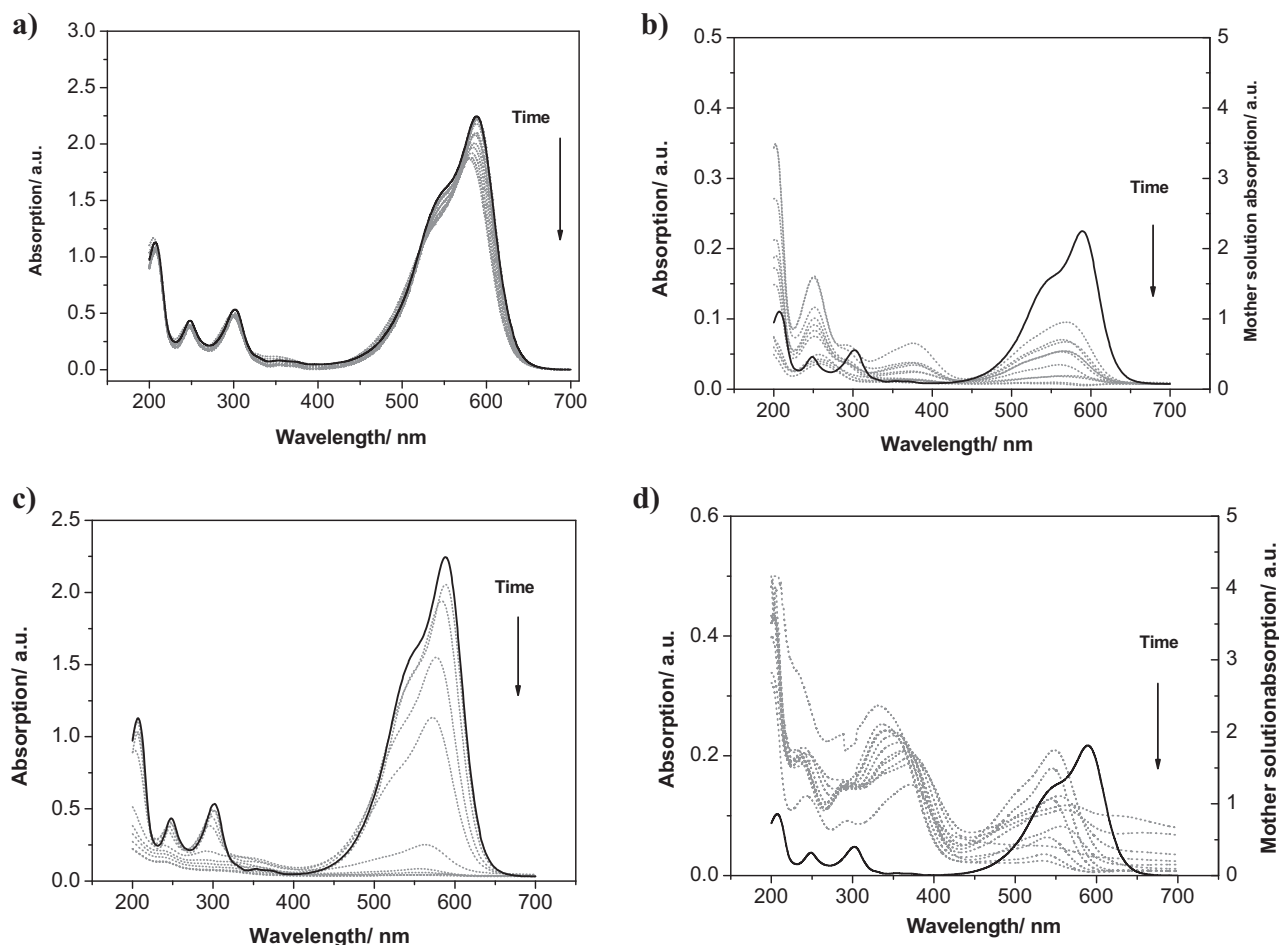


Fig. 4. Absorption spectra changes with time of CV in the (a) WAO (b) CWAQ of crystal violet at 120 °C, 50 bar and 100 ppm. Absorption spectra changes with time of CV in the (c) WAO (d) CWAQ of CV at 220 °C, 50 bar and 100 ppm.

were higher than those corresponding to wet air oxidation process in various orders of magnitude, at every temperature (Fig. 5a). It can be observed that an increase in the reaction temperature also improves the reaction rate. At 120 °C the reaction rate reaches $5.4 \times 10^{-4} \text{ mmol min}^{-1} \text{ g}_{\text{Ni}}^{-1}$, whereas at 220 °C the value attains

$1.3 \times 10^2 \text{ mmol min}^{-1} \text{ g}_{\text{Ni}}^{-1}$ for the catalytic test, showing that an increase of the temperature results in faster reactions.

Since TOC analysis only provides information about the removal of total organic carbon from the liquid-phase, selectivity towards non-organic compounds (S_{NOC}) was defined as $(X_{\text{TOC}}/X_{\text{dye}})$ where

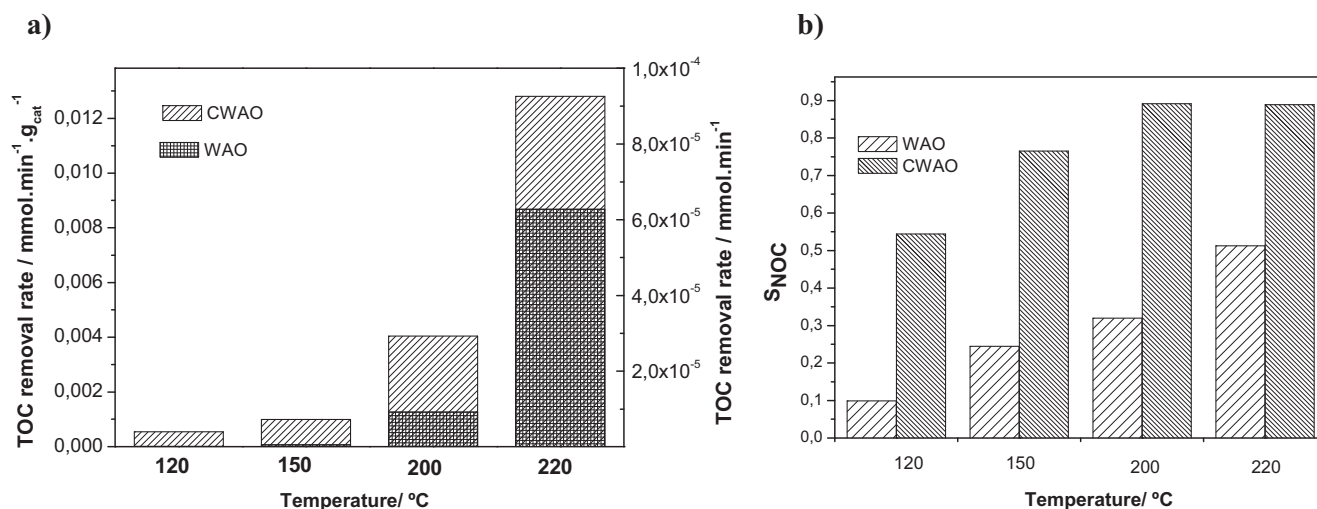


Fig. 5. Influence of temperature in (a) reaction rate (b) selectivity in WAO and CWAQ experiments at 50 bar 100 ppm.

Table 3

Toxicity units (TU) for WAO and CWAQ of crystal violet at 5 min and 15 min. Effect of temperature.

	WAO			CWAQ			Mother solution
	120 °C	150 °C	200 °C	120 °C	150 °C	200 °C	
TU 5 min	8.6	8.3	4.0	2.2	7.1	2.5	23.0
TU 15 min	8.2	8.3	4.5	2.1	6.7	1.2	21.0

X_{TOC} and X_{dye} are TOC and dye conversion respectively. Results are represented in Fig. 5b. Without catalyst, the selectivity towards non-organic compounds was always lower than catalytic tests, with a difference up to 60% at 220 °C. This reinforces the idea that the catalytic reaction goes through a different reaction pathway, in which reaction intermediates are more easily oxidizable than the ones for the non-catalytic reaction. It is worth noticing that in general, the higher the temperature the higher the selectivity, due to, as said before, the better carbon removal at high temperatures.

Table 3 shows the high toxicity of crystal violet. After the treatment, this value decreased remarkably with respect to the mother solution, being this abatement more important in the case of the CWAQ process. Besides, the lowest toxicity was attained for the highest temperature.

As a conclusion, higher temperatures are favorable for the CWAQ and WAO of crystal violet. However, higher temperatures translate into higher operating costs and more severe corrosion problems due to the presence of HCl generated during the reaction [20]. Additionally, it is important for this work that the reaction is operated under chemical control, in order to observe the effects of other operating parameters, the reaction should not be too fast either. Taking into consideration the above mentioned reasons, we have considered 150 °C as the optimum temperature for this study.

3.2.3. Effect of the pressure on the activity of Ni/HT in the WAO and CWAQ of CV

It has been found earlier that the oxygen partial pressure has some impact on both the conversion and the mineralization of the organic contaminants upon WAO [21]. This effect might be related to the amount of oxygen available in the active site [22]. Under our reaction conditions, oxygen solubility was approximately 0.12, 0.20, and 0.25 g L⁻¹ under 30, 50 and 65 bar, respectively. 15 bar of total pressure was calculated to be the minimum total pressure required for the complete oxidation of crystal violet to CO₂ and H₂O under the tested reaction conditions.

As shown in Fig. 6a, only a slight improvement for the WAO reaction with this variable was observed. On the other hand, the TOC abatement clearly improved as the total pressure increased (Fig. 6b). For the WAO reaction, this effect was evident when the total pressure increased from 50 to 65 bar while the difference between 30 and 50 was negligible. Above 65 bar, TOC conversion was not influenced by a pressure increase. This could be explained by a non-limiting oxygen diffusion in which the reaction is no more oxygen diffusion controlled but kinetic controlled [23].

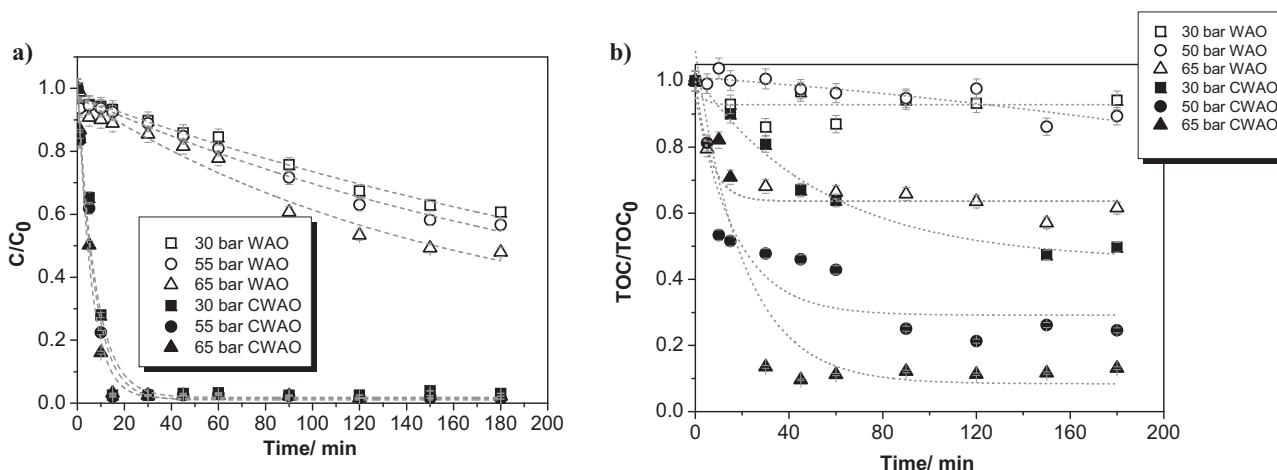
It can be stated that the oxygen concentration under the tested partial pressures was adequate for liquid-phase oxidation. It can be considered that oxygen concentration in higher partial pressure values than 65 bar was excessive with regard to organic matter.

As far as the initial reaction rate for the dye removal is concerned, WAO showed performances augmenting with total pressure from 1.1×10^{-7} to 7.3×10^{-7} mol min⁻¹ and for the CWAQ reactions these values ranged from 7.1×10^{-4} to 9.1×10^{-4} mol min⁻¹, showing that the presence of the catalyst enhances the initial degradation rate of the dye. The reaction order was calculated to be zero for the CWAQ reaction, showing that crystal violet abatement is not dependent on this parameter when catalyst is employed.

Fig. 7a shows that the ratio of initial TOC abatement is strongly dependent on the total pressure [24]. This implies that there are two limiting steps, the oxygen transfer from the gas to the liquid phase and from the liquid phase to the catalyst surface.

Selectivity is also influenced by total pressure, as shown in Fig. 7b. It is noticeable that at 65 bar the difference in the selectivity between WAO and CWAQ reaction is minimal, due to the best diffusion of the oxygen in the water at this pressure; a best oxidation of the reaction intermediates presents in the media is enabled.

Total pressure does not affect at the toxicity removal as much as temperature. Only a slight decrease in the toxicity of the final effluents was observed when the pressure increased.

**Fig. 6.** Evolution of the (a) CV (b) TOC conversion in the WAO and CWAQ at 150 °C and 100 ppm.

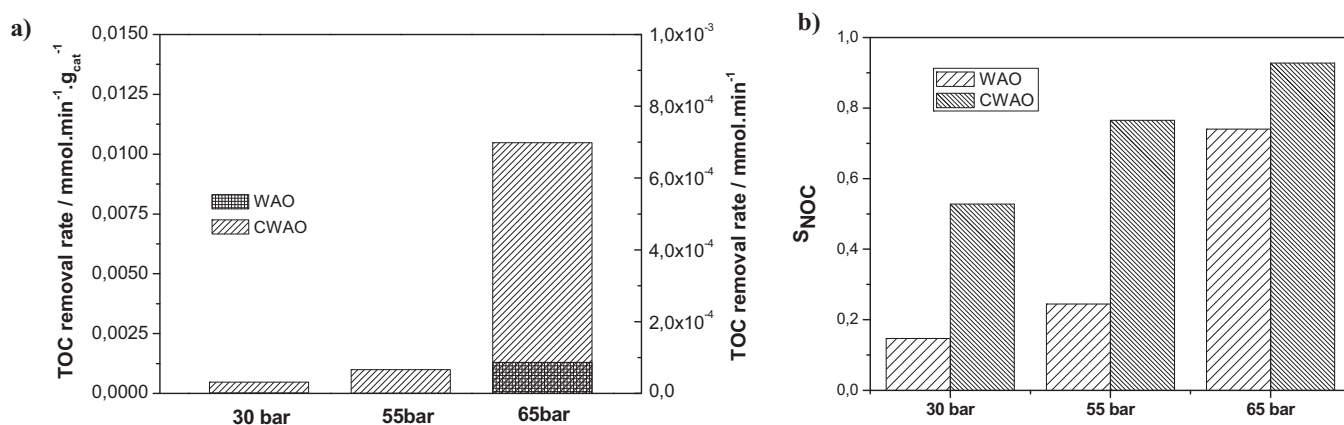


Fig. 7. Influence of total pressure in (a) TOC removal rate (b) selectivity in WAO and CWAO experiments at 150 °C, 100 ppm.

3.2.4. Effect of the initial CV concentration on the activity of Ni/MgAl in the WAO and CWAO of CV

Fig. 8a shows the results obtained upon the WAO and CWAO of crystal violet solutions (25 to 100 ppm) over the Ni/MgAl catalyst at 150 °C and 50 bar. Reaction rates are higher when the initial CV concentration augmented. Thus, for the WAO reaction initial reaction rate ranged from 4.6×10^{-7} to $7.4 \times 10^{-7} \text{ mol} \cdot \text{min}^{-1}$ and from 6.7×10^{-4} to $1.1 \times 10^{-3} \text{ mol} \cdot \text{min}^{-1} \cdot \text{g}_{\text{Ni}}^{-1}$ for the CWAO reaction were observed. This could be explained by an enhancement of the initial rate of the adsorption of the CV molecules onto the catalyst surface. The influence of the initial concentration of the reactant indicates that the reaction is controlled by the adsorption of the CV on the surface of the catalyst. Even though initial rate of TOC abatement is dependent on the initial concentration of the dye, final conversion of CV and TOC is not considerably affected by this parameter, as shown in Fig. 8a and b. This point has been observed by other authors as Li et al. [24].

As far as toxicity is considered, results are similar to those obtained for the variation of total pressure in the reactions, decreasing considerably with respect to the mother solution but showing no relevant differences when modifying CV initial concentration.

3.2.5. Effect of the pH on the activity of Ni/MgAl in the WAO and CWAO of CV

The effect of the pH on the efficiency and selectivity of the WAO and CWAO processes was studied. Experiments were carried out at

pH 2 and 11, and either HCl or NaOH was used to adjust the initial pH to the desired value.

CV removal was not affected by the pH media when the reaction was carried out with catalyst as it is shown in Fig. 9a. For the WAO reactions, a variation of the initial pH led to higher CV conversion, especially in an acidic media, due to the basic nature of the dye. In Fig. 9b it can be observed that the reaction at pH 2 showed worse performance than the reaction at its natural pH, obtaining conversions of 21% and 79%, respectively. Mikulová et al. [25] have proposed the formation of carbonate species and its deposition onto the catalyst surface as a cause of catalyst deactivation. As it was noticed by Li et al. [24] the inorganic carbon present in the reaction effluents was found to be high. This can be explained by the formation of carbonaceous species that could be easily adsorbed onto the catalyst surface and prevent the interaction between the solid and the organic compounds. Besides, as the Ni/MgAl is a basic catalyst, the addition of an acid solution could damage its adsorption properties.

On the other hand, for the WAO experiments, TOC removal rate is higher in an acidic medium, whereas the addition of NaOH seems not to have effects on the final conversion or on the reaction rate (Fig. 9b). On the opposite, the reaction at pH 2 showed the same performance than the reaction at its natural pH.

It is noticeable that the toxicity is higher for the experiments carried out at natural pH whereas TOC removal is lower when the pH was altered (Table 4). But according to the previous statements,

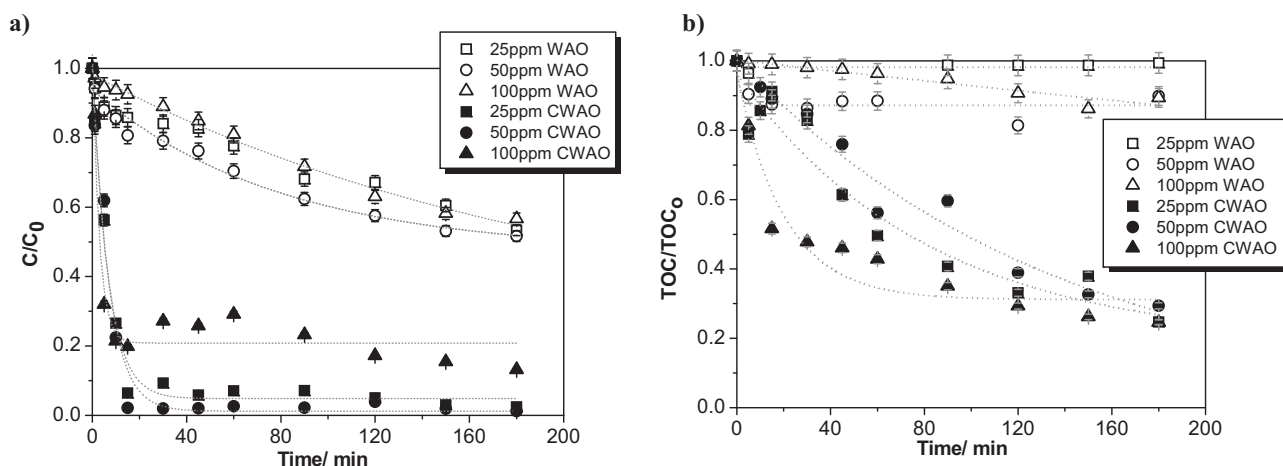


Fig. 8. Evolution of (a) CV conversion (b) TOC conversion in the WAO and CWAO at 150 °C and 50 bar.

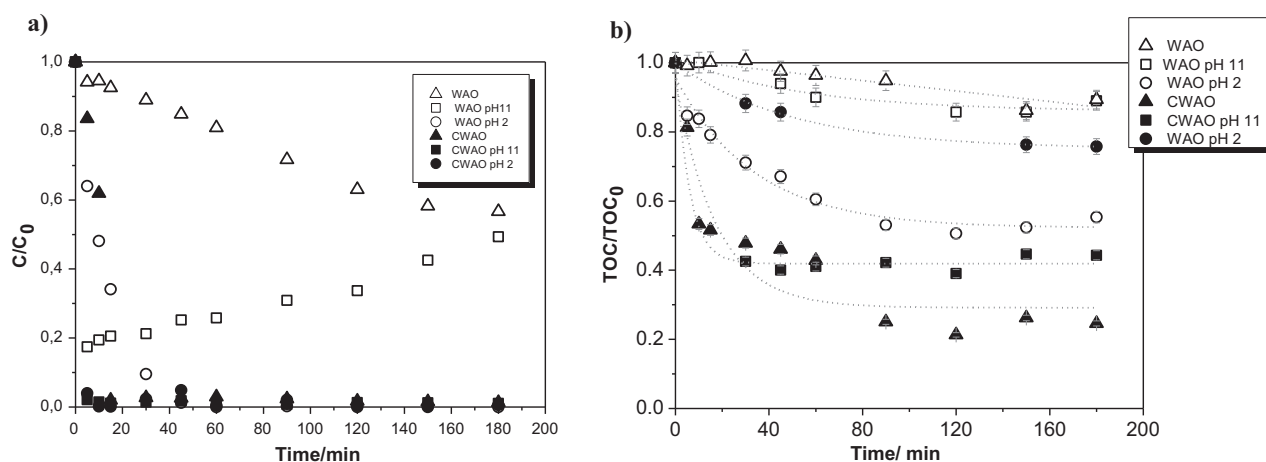


Fig. 9. Evolution of the (a) CV conversion (b) TOC conversion in the WAO and CWAO of CV at 150 °C, 50 bar and 100 ppm.

Table 4

Toxicity units (TU) for WAO and CWAO of CV at 5 min and 15 min. Effect of pH.

	WAO			CWAO			Mother solution
	pH 2	pH 11	pH natural	pH 2	pH 11	pH natural	
TU 5 min	1.9	2.4	8.3	1.4	0.6	7.1	23.0
TU 15 min	2.1	2.8	8.3	1.1	1.1	6.7	21.0

natural pH can be considered as the optimum one, which is convenient from a practical point of view, as far as no acid or base addition would be required in a post-treatment step.

3.3. Catalyst stability

Test on catalyst stability are primordial if we consider its industrial applications as well as for its potential toxicity if any component would be leached out.

For this reason, we have evaluated the catalyst performance by running three consecutive experiments recycling the catalyst. For this, after each experiment, the catalyst was separated from the effluents by filtering. Then the used catalyst was washed with water and dried for further reutilization.

It can be observed that Ni/MgAl catalyst does not lose any of its activity in the recycling experiments performed, when CV degradation is considered (Fig. 10a). On the other hand, if TOC

removal is considered (Fig. 10b), it can be noticed that there is no difference in the performance of the catalyst between the experiments carried out with the fresh catalyst and the first recycle, but there is a decrease of 10% in the final carbon conversion. One of the reasons for the deactivation of the catalyst might be due to the leaching of the nickel. The ICP-AES analysis of the final effluents and the solid samples revealed that only a 0.6% of the metal is leached from the support, so this hypothesis has to be rejected.

Another possible explanation to the observed facts is the formation of polymeric substances during the reaction [26]. This was confirmed by the measurement of the solid organic carbon deposited catalyst, by means of a Solid Sample Module SSM-5000A. Results showed that a carbonaceous deposit was formed on the catalyst, after the reutilization reactions, even if they have little effect on the performance of catalyst. However, experiments in a continuous trickle-bed reactor have been performed to confirm the

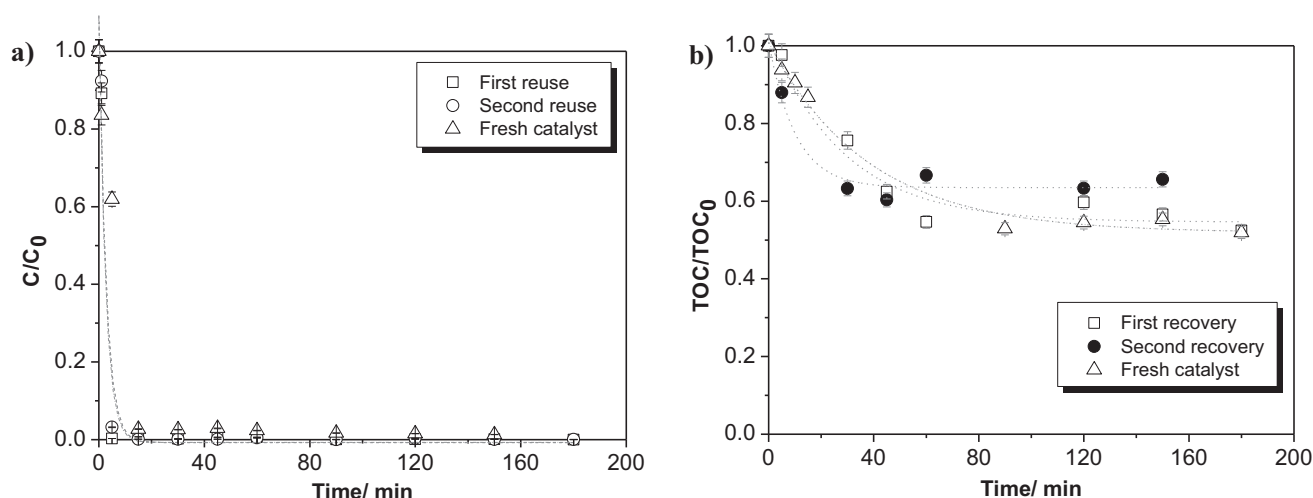


Fig. 10. (a) CV conversion (b) TOC conversion employing the recovered catalyst for WAO and CWAO at 150 °C, 50 bar and 100 ppm.

stability of the Ni/HT catalyst under the studied conditions and these results would appear on further publications.

4. Conclusions

It has been demonstrated that Ni/MgAl is an efficient catalyst for the CWAQ of crystal violet, leading to high conversion at mild reaction conditions. The activation energy was calculated to be 81.38 and 11.15 kJ mol⁻¹ for the WAO and CWAQ respectively, demonstrating the effectiveness of the catalytic process.

Temperature was the parameter, which showed the highest influence both in CV and TOC conversion. Additionally, the variation of the reaction parameters had more influence on the final conversion values when the experiments were carried out without the catalyst.

Finally the reaction which was carried out at its natural pH showed to be the most efficient when Ni/MgAl was employed, but achieved better results in an acidic media when the reaction was performed without catalyst.

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